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Authors

Baker, Bradly
Guenther, Alex
Greenberg, Jim
et al.

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Canopy Level Fluxes of 2-Methyl-3-buten-2-ol, Acetone, and Methanol by a Portable Relaxed Eddy Accumulation System

BRADLY BAKER,*,† ALEX GUENTHER, AND JIM GREENBERG

National Center for Atmospheric Research, Boulder, Colorado 80303

RAY FALL†

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309

Canopy level flux measurements of 2-methyl-3-buten-2-ol (MBO), acetone, and methanol were made over a subalpine forest in the Rocky Mountains in Colorado in the summer of 1999. The measurements were carried out using a portable relaxed eddy accumulation system that collected samples on adsorbent cartridges. Midday fluxes of acetone were highest at ~2.5 mg of C m^{-2} h^{-1}. Methanol and MBO fluxes were ~1.0 mg of C m^{-2} h^{-1} each. These fluxes occurred with average daytime high temperatures of only 18 °C. Diurnal fluxes of MBO were strongly correlated with light and temperature. Acetone and methanol did not have simple diurnal patterns. These results indicate that oxygenated volatile organic compounds may make a significant contribution to the flux of reactive carbon to the atmosphere in western U.S. pine forests.

Introduction

Volatile organic compounds (VOCs) emitted from the biosphere play important roles in the chemical processes of the troposphere. These processes include the photochemical production of ozone in both rural and urban atmospheres (*1*, *2*) and influences on other atmospheric oxidants and aerosols. Model calculations suggest that about 1150 Tg of carbon is emitted into the atmosphere every year in the form of biogenic VOCs from vegetation (*3*). The largest uncertainties in biogenic VOC emission inventories are associated with oxygenated VOCs such as methanol and acetone. There are few published reports that detail fluxes of these compounds. Methanol and acetone were the two most abundant VOCs measured above several different forest ecosystems (*4*−*6*). Other studies, carried out with intact plants, have shown that methanol (*7*, *8*) and acetone (*9*−*12*) are biogenically produced, and it is now clear that wounded stems and leaves also release these and other oxygenated VOCs (*10*, *13*, *14*). Interest in biogenic acetone arises from the belief that acetone could be a significant source of HO_x in the upper troposphere (*15*). Methanol may have important implications with respect to atmospheric formaldehyde in some regions. In the western United States, the oxygenated compound 2-methyl-3-buten-2-ol (MBO) may be the predominant reactive VOC above certain pine forests (*16*−*19*).

Until recently, most studies of biogenic VOCs have consisted of ambient measurements of compounds above a vegetation source. Biogenic sources have been determined by correlation with environmental variables such as light and temperature or by correlating the diurnal pattern with another VOC that is of known biogenic origin, while anthropogenic sources have been determined by correlation with common anthropogenic tracer compounds such as benzene and toluene. While these measurements are useful in examining atmospheric chemistry, give clues as to sources of VOCs, and can be used to roughly model fluxes, they do not help us determine an accurate source strength or flux of a compound to the atmosphere. Knowing an accurate flux is vital for both developing and verifying models that predict regional and global emissions of biogenic VOCs.

Canopy-level flux measurements of biogenic VOC are complicated by the fact that fast sensors (1 Hz and faster) are not available for many hydrocarbons, thus making direct measurements of flux using eddy covariance techniques impossible. Even when a fast sensor is available as is the case with isoprene (*20*, *21*), the amount of equipment and power requirements can be cumbersome for a remote field site. Relaxed eddy accumulation (REA) has been developed as a means to eliminate the need for a fast sensor when measuring trace gas fluxes (*22*). This paper describes a portable REA system that is able to measure a wide range of VOC fluxes, including oxygenated biogenic VOCs, such as MBO, methanol, and acetone.

Experimental Section

REA System. The theory behind REA is explained elsewhere (*22*). In short, two air samples are collected over a statistically meaningful time period (~30 min); one consisting of updrafts and one consisting of downdrafts. Although sampling alternates between up and down reservoirs, it occurs at a constant flow rate. The duration of sample collection for each reservoir is related to the frequency at which the wind eddies change vertical direction. The flux (F) is then calculated using the following relationship:

$$F = \beta\sigma_w(C_u - C_d) \quad (1)$$

The value β is a unitless coefficient, which in completely ideal conditions (e.g., over a smooth surface) has a value of 0.6 but can also be determined empirically (*23*). The standard deviation of the vertical wind over the collection period is σ_w, and C_u and C_d are the average concentrations of the analyte of interest in the up and down reservoirs, respectively. To increase the sensitivity of the measurement, it is common to include a dead band in the sampling at which time the sample air is vented, and no sampling occurs when the vertical wind velocity does not exceed a preset value in either the up or the down direction. The result is that the empirical determination of β is less than 0.6, and there is a larger difference in concentration between the up and the down reservoirs.

The REA technique has been used to measure biogenic VOC fluxes in the past (*24*−*26*, *18*). There are two basic system designs. Most common is the bag-type REA in which the up

* Corresponding author present address: Institute of Atmospheric Sciences, South Dakota School of Mines and Technology, 501 East St. Joseph, Rapid City, SD 57701; phone: (605)394-6997; fax: (605)-394-5360; e-mail: Brad.Baker@sdsmt.edu.

†Also at the Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309.

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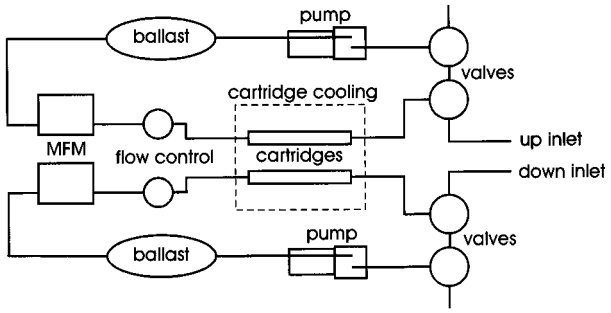

FIGURE 1. Schematic diagram of the cartridge relaxed eddy accumulation system. MFM is mass flow meter.

and down reservoirs consist of Teflon or Tedlar bags (*24*, *26*, *18*). The air sample is drawn through a pump and then directed by valves to one or the other of the bag reservoirs depending on the vertical wind measurement. The advantage of this system is that there is little or no pressure drop between the inlet and the reservoirs, so maintaining a constant sampling rate is not difficult. The major disadvantage of this system is that sample analysis must be done on site since bags are not a good long-term storage container for sampled air. This is due to their awkwardness, artifacts coming from the bag material, adsorption of compounds onto the bag material, and potential for leaks. Samples could be transferred from bags to adsorbent cartridges or canisters; however, this would increase the chance for artifacts and sample loss to occur. Consequently, a gas chromatograph (GC) system must be set up at the sampling site, and a GC is both a large consumer of power and difficult to deploy at more remote sites. The other system type is the cartridge REA in which the reservoirs consist of tubes packed with an adsorbent material that collects the analytes as the ambient air passes through. The advantage of the cartridge REA is that samples are contained in a small, lightweight portable container that can easily be taken back to the lab and analyzed. The specifics of the cartridges used with the REA described in this paper are discussed below. The primary difficulty with a cartridge REA is that there is a pressure drop across the sampling reservoir. This makes it difficult to maintain a constant flow when sampling is switching between the two reservoirs at a high frequency. Methods have been developed to maintain the pressure drop across the reservoir during off sampling times; however, this requires techniques such as having zero air flowing through the off cartridge, which requires having a tank of zero air or producing zero air on site (*27*). A discussion of both these types of REAs, and particularly the bag REA, is found in ref *26*.

The cartridge REA system described here (Figure 1) was designed to maintain the pressure drop across the sample reservoirs, while avoiding the need for having zero air on site. The up and the down sampling inlets were independent of each other. During sampling, air was drawn by a pump through both inlet lines. Prior to encountering the pump, the samples ran through a three-way Teflon isolation valve (Bio-Chem Valve Inc., Boonton, NJ; response time of <20 ms) and then flowed through the sample reservoir or cartridge where all of the hydrocarbons were collected from the airstream. After leaving the cartridge, the filtered airstream ran through a bellows metering valve (Nupro, Willoughby, OH), a mass flow meter (MFM) (Micro Switch, Freeport, IL; model AWM3300; response time of 5 ms), a ballast volume, and the Teflon diaphragm pump (KNF Neuberger, Princeton, NJ; model NPH 30) and finally exited through another valve to vent. During off sampling periods, both valves were switched, and air already scrubbed of hydrocarbons by the sampling cartridges recirculated through a closed loop, thus maintaining the pressure drop across the sample reservoir. All tubing was PFA Teflon, including the fittings on each side of the cartridge, and the ballast volume consisted of approximately 50 cm of 0.25-in. Teflon tubing packed loosely with glass wool. The purpose of the ballast was to dampen out oscillating flow from the diaphragm pump. Analysis of zero air passed through the REA showed no measurable trace of the target compounds. Mass flow through the system measured by the MFMs was read on a panel display (Datel, Mansfield, MA) so flows could be adjusted in situ using the bellows metering valves. The limiting pressure drop was across the bellows metering valve, so once a flow was set, it remained constant from one sampling period to another, regardless of the pressure drop across the cartridge. The cartridges were housed in a cooling unit so sampling could take place at subambient temperatures. The unit was cooled by two three-stage peltier coolers (Melcor Thermoelectrics, Trenton, NJ; model 3CP 085 065-71-31-17L) controlled by a standard controller unit (Omega, Stamford, CT). Temperatures as low as -30 °C were reached. Valve switching was controlled by a laptop computer with a PCMCIA acquisition and control board (National Instruments, Austin, TX) that acquired wind data from a 3D sonic anemometer (Applied Technologies, Boulder, CO) operating at 10 Hz. During sampling periods, the sample was first drawn through an ozone scrubber placed at the end of each inlet line. The scrubbers consisted of a 0.25 in. (0.64 cm) o.d. glass tube, 4 cm long, packed with glass wool impregnated with potassium iodide (*18*, *28*). For this experiment, a dead band was set for wind velocities not exceeding $0.6\sigma_w$ (*29*), in which case both up and down channels were recirculating air. The value of σ_w was determined based on the vertical wind from the previous 0.5-h period. The constant β was determined by measuring heat flux by eddy covariance. The dead band was taken into consideration in this calculation (*18*). The REA system (not including the computer and sonic anemometer) was housed in a box 50 cm $\times$ 43 cm $\times$ 23 cm and weighed 13.5 kg. Maximum power consumption was 120 W. The major consumption was by the peltier coolers; if they were not used, power consumption was 60 W.

To check if the flow rate through the REA was truly constant, the recorded MFM data was examined. Figure 2 represents the recorded flow during a 0.5-h sampling period above the forest canopy for the up and down loop of the REA. Only data from sampling periods (no data from deadband periods) during the 0.5 h are displayed. The data represent the output of the MFMs that were calibrated using a bubble flow meter (Gillian Corp., Wayne, NJ) both before and after the field experiment. No change in the calibration occurred between these two times. Figure 2 shows that during a typical sampling period the flow remained constant to within a relative standard deviation of less than 8% for both the up and the down channels.

The REA system's response time to changes in vertical wind direction was not directly tested. The switching frequency was controlled by the 10-Hz data received by the sonic anemometer. The valves and MFMs had response times much faster than 10 Hz, so it was assumed that the system responded with less than a 0.1-s delay. No offset was programmed into the system, as has been done for single inlet REAs (*26*) to account for the time that the sample takes to get from the sample inlet to the segregation valve. In the REA system described here, each channel of the REA had a separate inlet, and only up eddy air went to the up cartridge and vice versa. It has also been shown that even over a relatively open pine forest canopy, offset errors of more than a few tenths of a second produce small flux errors (*18*). To examine the potential for flux errors due to a system response slower than 0.1 s, the vertical wind data from a typical 0.5 h of sampling was plotted (Figure 3) to show the cumulative density of sampled turbulent eddies as a function of eddy

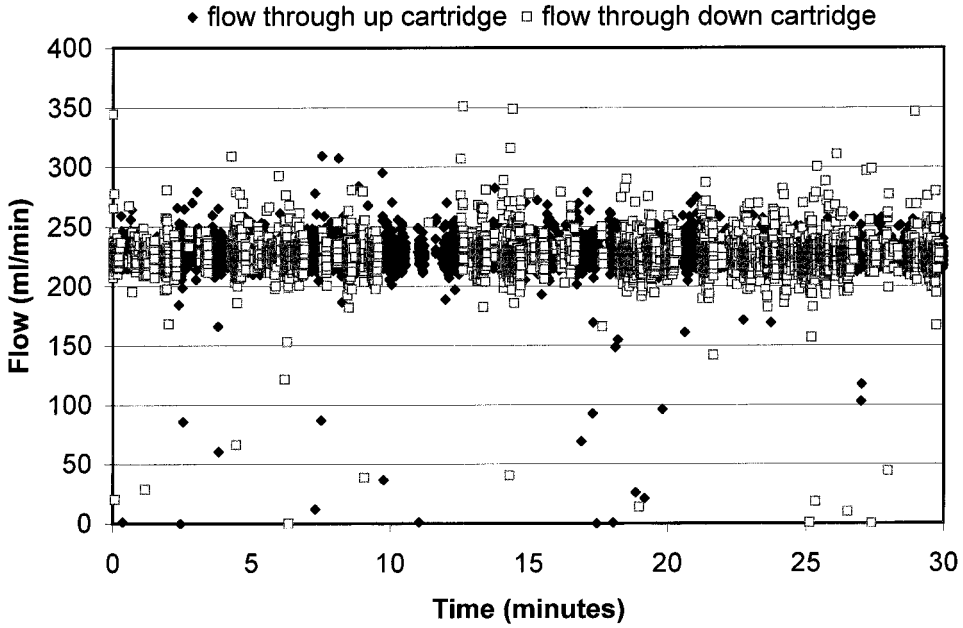

FIGURE 2. Mass flow meter output from the relaxed eddy accumulation system showing the constant flow rate through both the up and the down cartridge during sampling periods. Each data point represent one-tenth of a second.

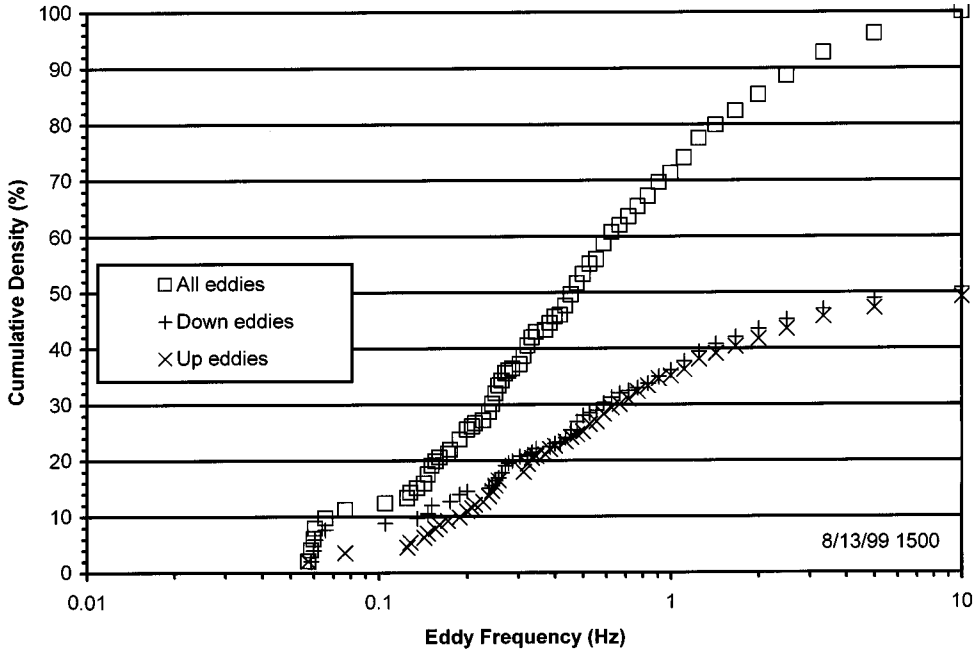

FIGURE 3. Cumulative density of sampled turbulent eddies as a function of eddy frequency for a typical 0.5-h sampling period at the Niwot Ridge subalpine forest. High frequency eddies faster than 2 Hz account for only 10% of the flux.

frequency. Figure 3 reflects the eddies that the REA sampled, i.e., the sampling dead band was factored in. This type of analysis has been made in the past for vertical winds over a mixed deciduous forest to show that an instrument response time of 2 Hz was fast enough to adequately measure isoprene fluxes (*21*). Figure 3 shows that the eddies with frequencies higher than 0.25 Hz account for less than 10% of the total amount of air moved by turbulence over the subalpine coniferous forest where this study took place. Response delays of up to 0.5 s would translate into missing about 10% of the flux.

Cartridges. Adsorbent cartridges have been used successfully for the measurement of trace VOCs in the atmosphere (*30, 31*). The cartridges used with this system (Supelco, Bellefonte, PA) were constructed of 3.5 in. (8.9 cm) long by 0.25 in. (0.64 cm) o.d. Silcosteel tubes packed with 350 mg of Carbotrap followed by 180 mg of Carbosieve S-III. Sampling was done in such a way that compounds encountered the Carbotrap first, and desorption of the cartridges was in the opposite direction as sampling. To prepare for sampling, the cartridges were heated to 300 °C for approximately 12 h with a 75 mL min^{-1} flow of UHP nitrogen. Cartridges were kept refrigerated at −30 °C in the lab, both before and after field sampling. In the field, cartridges were kept packed in dry ice (−80 °C). Our experience has suggested that keeping cartridges at subambient temperatures during storage, both before and after sampling, helps in reducing the background of some compounds in the blank (*32*). In addition, keeping cartridges cool after sampling helps prevent the loss of some VOCs during storage times of days to weeks.

During sampling, cartridges were also kept at subambient temperatures. For this experiment, the cartridge cooler on

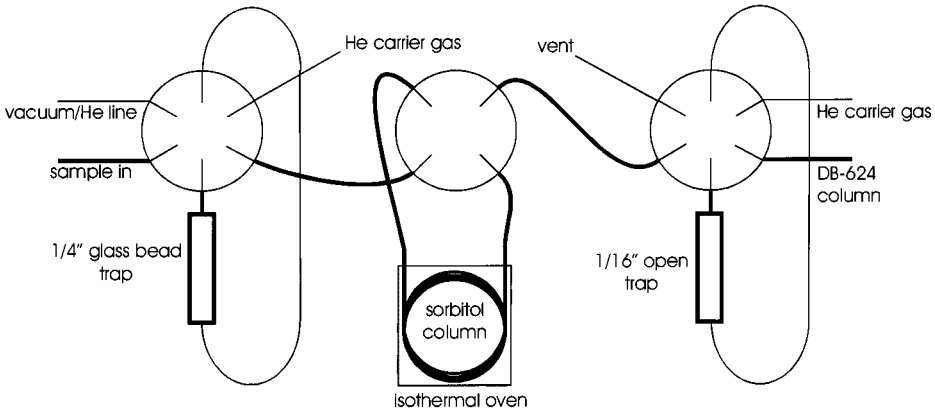

FIGURE 4. Schematic diagram of the gas chromatography inlet system used to analyze the cartridges from the relaxed eddy accumulation system. Darkened lines indicate the sample path through the system.

the REA was set to −15 °C. The reason for this is 2-fold. First, the breakthrough volume for all compounds is substantially increased at lower temperatures. Since air was continuously passing through the cartridge in this REA, it was important to maximize the breakthrough volumes. However, for this experiment, no more than 10 L of air ever passed through a cartridge, and at −15 °C, breakthrough volumes for the target compounds are much greater. Second, when atmospheric water vapor is present, the breakthrough volumes for highly polar compounds such as methanol are greatly reduced. To collect all of the methanol and other polar compounds on the cartridge, temperatures below 0 °C must be used. We have seen this occur with a wide variety of adsorbent types. However, high concentrations of water in the sample have the potential to cause problems with the VOC analysis.

VOC Analysis. Water, in high concentrations, can freeze and restrict flow in cryoenrichers, interfere with and degrade separations, and extinguish the hydrogen flame in a flame ionization detector (FID). Many methods have been devised to remove water from atmospheric samples before preconcentration and injection to the GC column (*33*). Most of these methods, while effectively separating water from most atmospheric trace gases of interest, do not separate water effectively from highly polar VOCs such as methanol. Instead, these VOCs are removed from the sample along with the water, and quantitative results are much more difficult. One method for separating water from the more polar atmospheric trace VOCs that has been used with success is two-dimensional chromatography (*34*, *35*, *5*). We have employed similar methods in the analysis described below.

Sampled cartridges were analyzed within 2 days of sample collection. Samples were introduced to the GC system by sending ∼50 mL min^{-1} of He through the cartridge in the opposite direction as sampling for 8 min while heating the cartridge rapidly to 280 °C by clamping on a preheated brass block. The inlet of the GC system is shown in Figure 4 and was based on a system described in ref *5*. Helium carrying the sample from the cartridge first encountered an enricher that consisted of a 0.25 in. (0.64 cm) o.d. Silcosteel tube packed with glass beads (60/80 mesh) immersed in liquid nitrogen. After the sample was concentrated on this enricher, it was back-flushed onto a sorbitol column (Alltech Associates, Inc., Deerfield, IL; 2 m × 0.125 in. (0.32 cm) o.d. Silcosteel, 25% sorbitol on 80/100 mesh GasChrom QII) by heating with a sand bath at 250 °C. Sorbitol strongly retains water, allowing the rest of the sample, including methanol, to elute through and be focused on the second enricher. The sorbitol column was kept in an isothermal oven at 105 °C with a carrier gas flow rate of 25 mL min^{-1} He. The flow through the sorbitol column was then reversed after 14 min, and the water was back-flushed off of the column before the next analysis. The second enricher consisted of a 0.0625 in. (0.16 cm) o.d. Silcosteel open tube immersed in liquid nitrogen. The enricher was placed in-line with the carrier gas and heated to 250 °C in a sand bath to inject the sample onto the analytical column. All tubing that the sample contacted in the system was constructed of Silcosteel and heated to 100 °C.

The primary analytical column used was a DB-624 (J & W, Folsom CA, 30 m × 0.32 mm i.d., 1.8 μm film thickness). The DB-624 column is a mid-polarity column, which is useful in the analysis of both polar and nonpolar trace gases. It also has the potential of separating C_2−C_4 hydrocarbons without the need for subambient temperature programming. The temperature program began at 30 °C for 6 min, then ramped to 100 °C at 10 °C min^{-1}, and then ramped to 200 °C at 20 °C min^{-1}. Detection of compounds was achieved by a FID.

Calibration. Instrument calibration occurred on each day that sample analysis took place. The standard consisted of a commercially prepared compressed gas mixture that contained a number of VOCs in the parts per million range including MBO, acetone, and methanol (Scott-Marin, San Bernadino, CA). Dilution of this standard was carried out using a dynamic dilution system that consisted of several mass flow controllers (Tylan Corp., San Diego, CA; Unit Instruments Inc., Yorba Linda, CA) used to precisely mix the standard gas with hydrocarbon free air and produce a gas stream with MBO, acetone, and methanol concentrations on the order of a few parts per billion. Zero air used to dilute the standard was partially humidified before mixing with the standard gas to simulate atmospheric water vapor concentrations. Calibration of the standard cylinder is described in ref *18*. Standards were collected in the laboratory at −20 °C on the same cartridges used in the field for sample collection and were analyzed in the same way as field samples. Percent standard deviation of standards over the course of the 40-day period in which analysis took place was 10% for acetone, 15% for MBO, and 20% for methanol. Average response by the FID to the standards decreased by 5% over the course of the 40 days. To test for the cartridge to cartridge variation in field samples, ambient measurements were periodically made at the field site using both channels of the REA instrument to sample simultaneously. For these sample pairs, the average difference in concentrations was 3% (1σ = 55%) for MBO, 7% (1σ = 83%) for acetone, and 17% (1σ = 100%) for methanol. This comparison represents four sample pairs collected on two early mornings and two afternoons. The better reproducibility in the field data versus the standards was attributed to problems with pump fluctuations in the apparatus used to collect the standards onto cartridges in the lab.

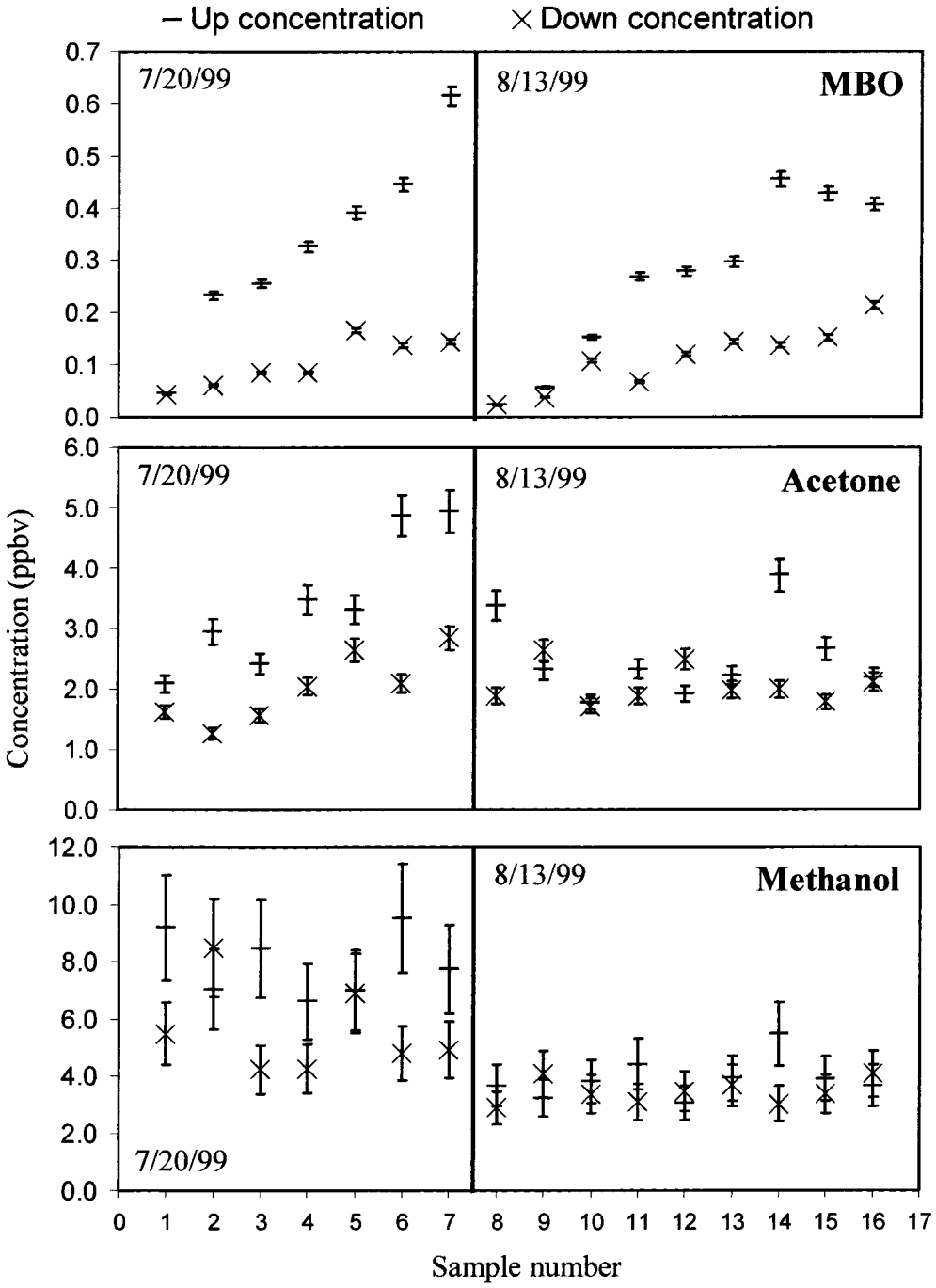

FIGURE 5. Comparison of the measured concentrations of 2-methyl-3-buten-2-ol, acetone, and methanol for the up and down reservoirs for each relaxed eddy accumulation sample taken on July 20 and August 13, 1999. The error bars represent the precision (1σ) with which the determination of the concentration of each compound could be made.

Sampling Site. Measurements were made from a 25 m tall walk-up tower at the Niwot Ridge Ameriflux site located in the Arapahoe National Forest in Colorado (40°01′58.4″ N, 105°32′47.0″ W, 3050 m above sea level) on several days during the months of July and August 1999. The forest was accessed through the University of Colorado Mountain Research Station. The footprint of the flux measurements consisted of a mature stand of 43% lodgepole pine (*Pinus contorta*), 35% subalpine fir (*Abies lasiocarpa*), and 22% engelman spruce (*Picea engelmannii*) (by basal area) situated on a slope of 6°, which slanted up toward the Continental Divide to the west. The height of the canopy was ~15m. This site is well-suited for the measurement of MBO fluxes since it has been shown that lodgepole pine are a high emitter of MBO (*17*) and should be the predominant reactive hydrocarbon over this forest. Characteristic morning winds at the site were downslope and westerly. Shortly after noon, the winds would usually switch to easterly and upslope, frequently accompanied by thundershowers. During days on which sampling took place, daytime high temperatures averaged 18 °C with a high of 19 °C. Light levels reached 2000 μmol m^{-2} s^{-1} of photosynthetically active radiation (PAR) at midday. Sample inlets for the REA were placed at 19 m on the walk-up tower. All data presented here are from times of downslope winds from the Continental Divide.

Results and Discussion

Flux Measurements. Reported measurements were made in the morning hours during downslope wind conditions and before afternoon thunderstorms moved in. Only data

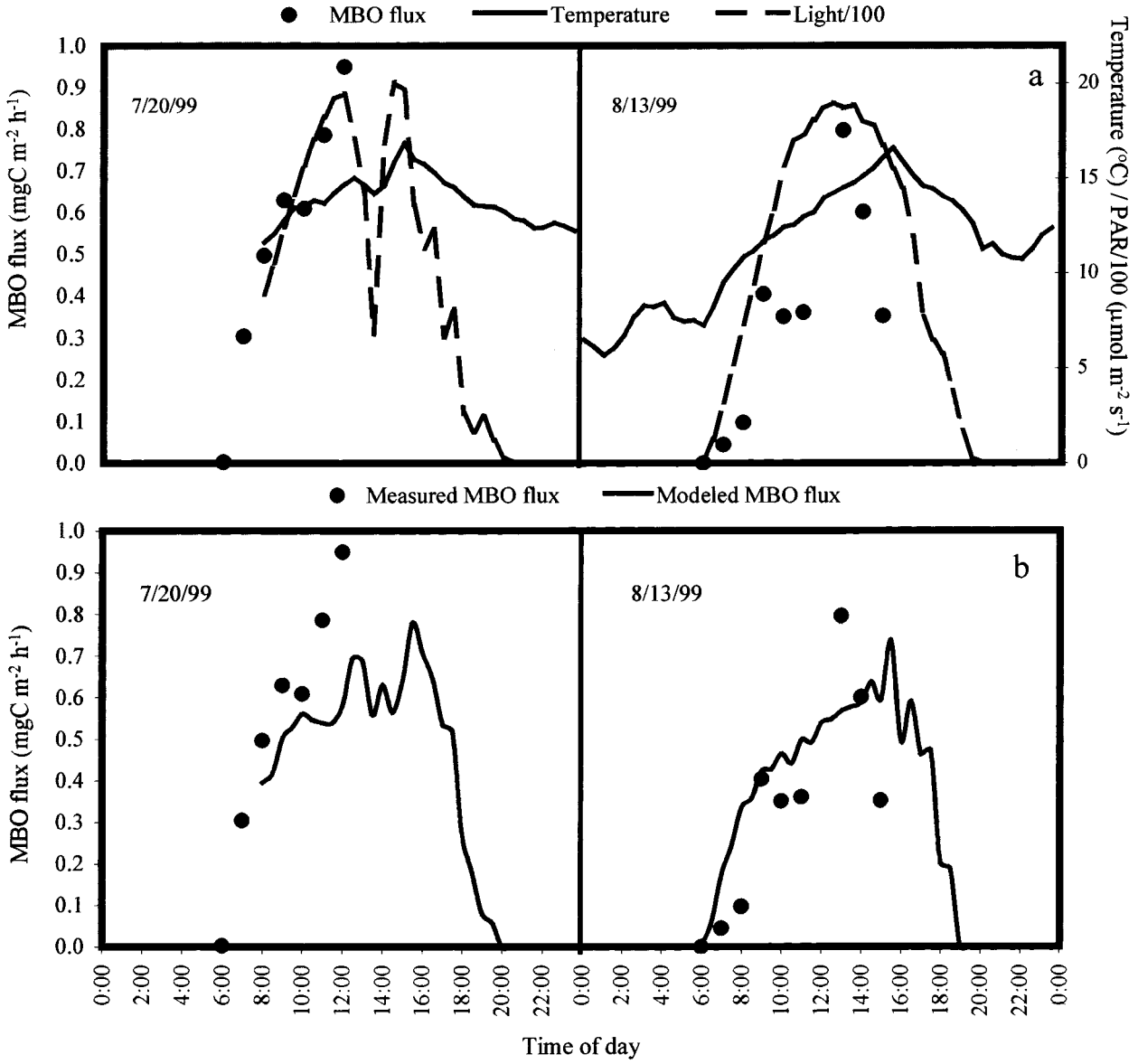

FIGURE 6. (a) 2-Methyl-3-buten-2-ol fluxes for two independent days with those days' light and temperature data. (b) Modeled fluxes along with the measured flux for comparison.

from the 2 days of sampling in which relatively continuous samples were acquired are presented here. Figure 5 compares the measured concentrations of the up and the down cartridges for MBO, acetone, and methanol on July 20 and August 13, 1999. The error bars represent the uncertainty in the analytical determination of the concentration of each compound of interest. Differences in the up and the down MBO concentrations are quite large vs the uncertainty in the measurement, and the uncertainties in the overall flux measurements are low. For acetone, the uncertainty relative to the concentration difference is greater, but a flux is still able to be determined. The pattern of methanol fluxes cannot be precisely determined, especially on August 13, when the observed fluxes were relatively low as compared to July 20. However, we report the methanol fluxes anyway since it indicates an upper limit to what the fluxes were. It is worthwhile to note that high temperatures did not exceed 19 °C on the two days when fluxes are reported. Fluxes at this low temperature will not be nearly as high as what might be expected from a forest in a warmer climate.

MBO Fluxes. The data shows a definite diurnal pattern in the flux of MBO with maximum fluxes at midday. This has also been seen over a ponderosa pine canopy (*18*), and it has been shown that MBO emissions are largely controlled by light and temperature at the needle level (*17*). Figure 6a shows MBO flux measurements for July 20, August 13, and each day's light and temperature data. Light and temperature data were not available for the morning of July 20. The landscape emission model of ref *3* was used to model emissions of MBO over the pine forests of the Front Range in Colorado. It has been suggested that MBO fluxes from pines can be modeled at the needle level using the same algorithms that were devised for biogenic isoprene emission (*17*, *36*). The same model was used to compare the canopy level emissions of MBO from a ponderosa pine plantation in the Sierra Nevada Range of California with REA flux measurements and came up with values a factor of 2 higher than the measurements; however, model and measurements followed the same general diurnal pattern (*18*). Here we used the same parameters as ref *17* to model MBO emissions at the Niwot Ridge site using the temperature and light data that were collected during this experiment.

Figure 6b shows the modeled and measured MBO flux for July 20 and August 13. The modeled fluxes underestimated

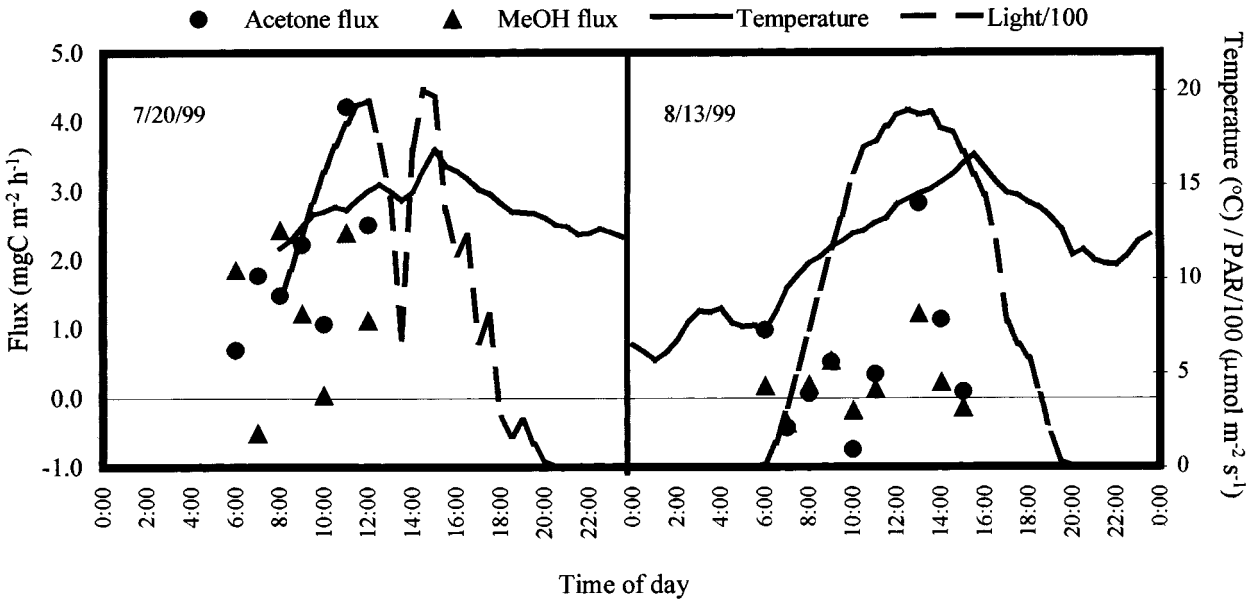

FIGURE 7. Acetone and methanol fluxes for two independent days (as in Figure 6a for MBO) with those days' light and temperature data.

the measured fluxes by less than 10%, however, with a standard deviation of 50%. The scatter is probably due to several causes. As discussed in ref *18*, on short time scales, the model only accounts for changes in the emissions due to changes in light and temperature. Variations in the measured flux due to a changing footprint region and other environmental variables may have had an effect on MBO emissions within time scales of 0.5 h.

Acetone and MeOH Fluxes. For acetone and methanol, the pattern of emissions was not clear. Figure 7 shows fluxes of acetone and methanol for July 20 and August 13. There was no apparent correlation between emissions of these two compounds and light and temperature. Emissions on August 13 were on average lower than those of July 20, although maximum temperature and light between the two days was not significantly different, suggesting that some other variable was controlling these emission rates. In some cases there seemed to be deposition to the forest. One should be reminded that the precision of the acetone and especially the methanol flux measurements were not as great as that for MBO, such that the measured negative fluxes may have been due to imprecision in the measurements. Methanol emissions from broad-leafed plants seemed to follow stomatal conductance rather than temperature; however, no measurements have been made on pine plants (*7*, *8*). It is believed that methanol is emitted by trees during periods of rapid leaf or needle growth. Acetone may be emitted from conifer buds (*9*); however, our studies have shown that acetone may also be emitted directly from pine needles of some species (unpublished data) and appeared to follow the emission pattern of MBO quite closely under certain light and temperature conditions. Describing patterns of canopy level fluxes of acetone and methanol is further complicated by the possible emission of these compounds from wet soils and leaf litter (*37*).

Boundary Layer Mass Balance Model. The oxygenated VOC emissions estimated for this site using the REA system should have a significant impact on atmospheric concentrations of these compounds. As a constraint on the REA flux estimates, a simple mass balance box model was used to predict the late morning concentrations expected for the fluxes measured by REA. The model predicted the absolute concentration for a short-lived compound (e.g., MBO) and the rate of concentration change for long-lived compounds (e.g., methanol and acetone). The model assumes that

$$\Delta C = \frac{\overline{(wc)_o} + z_i PC_i - \overline{(wc)_n}}{zL} \qquad (2)$$

where ΔC is the change in concentration for the compound of interest; $\overline{(wc)_o}$ and $\overline{(wc)_n}$ are the surface flux above the canopy and the entrainment flux, respectively; z_i is the height of the mixed layer, PC_i is a production term due to the concentration (C_i) of a precursor compound, and L is the loss term due to OH and ozone. The general model assumptions and associated uncertainties are discussed by ref *24*. We assumed a midday boundary layer height of 1 km, an OH concentration of 3×10^6 molecules per cm^3, and an ozone concentration of 50 ppbv based on measurements at a nearby site (*38*). The model includes the production of methanol from methane; the production of acetone from propane, monoterpenes, and MBO; and the entrainment of VOC from above the boundary layer. For the observed surface emissions of 1 mg of C m^{-2} h^{-1} of MBO and methanol and 2.5 mg of C m^{-2} h^{-1} of acetone, we estimate a boundary layer average midday MBO concentration of about 200 pptv and concentration changes of 500 and 600 pptv h^{-1} for methanol and acetone, respectively. In comparison, we observed 400 pptv MBO and concentration changes of 1500 and 600 pptv h^{-1} for methanol and acetone, respectively, in the surface layer. The surface layer tends to have concentrations that are about 50−100% higher than the boundary layer average for reactive VOC that are emitted from the surface (*24*).

We have observed significant fluxes of three oxygenated VOCs over a pine forest in the Front Range of the Rocky Mountains in the United States measured with an easily deployable flux measurement system. Very few studies have been made to quantitate the fluxes of these and other oxygenated VOCs from biogenic sources. Although it appears that the importance of MBO may be limited to pine forests of the western United States (*17*), acetone and methanol may have important biogenic sources globally. A simple model calculated that 20% of the acetone measured in the free troposphere comes from biogenic sources (*15*). Ambient concentrations of MeOH measured over forested regions (*4*−*6*) cannot be accounted for by nonbiogenic sources. Our understanding of the role these compounds play in atmo-

spheric chemistry depends on the understanding and quantification of the biogenic emissions. Obtaining flux measurements of these and other biogenic VOCs depends on having instrumentation that is portable and requires little power so that it can be deployed in remote regions such as many areas in the tropics where net primary productivity is the highest. Future improvements in analytical methods need to focus on greater precision and speed in measuring oxygenated VOCs such as acetone and especially methanol.

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